

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/30, 3/37	A1	(11) International Publication Number: WO 99/14297 (43) International Publication Date: 25 March 1999 (25.03.99)
(21) International Application Number: PCT/US98/19140 (22) International Filing Date: 15 September 1998 (15.09.98) (30) Priority Data: 60/058,810 15 September 1997 (15.09.97) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PANANDIKER, Rajan, Keshav [US/US]; 6484 Oregon Pass, West Chester, OH 45069 (US). RANDALL, Sherri, Lynn [US/US]; 6841 Stone Valley Court, Hamilton, OH 45011 (US). GOSSELINK, Eugene, Paul [US/US]; 3754 Susanna Drive, Cincinnati, OH 45251 (US). WERTZ, William, Conrad [US/US]; 1273 Morgan Road, West Harrison, IN 47060 (US). HILDEBRANDT, Soren [DE/DE]; Remlingerstrasse 24, D-67343 Speyer (DE). KAPPES, Elisabeth [DE/DE]; Mainstrasse 2, D-67117 Limburgerhof (DE). BOECKH, Dieter [DE/DE]; Zeppelinweg 3, D-67117 Limburgerhof (DE).		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). (81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LAUNDRY DETERGENT COMPOSITIONS WITH LINEAR AMINE BASED POLYMERS TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO FABRICS LAUNDERED THEREWITH (57) Abstract Compositions and methods which utilize certain linear amine based polymer, oligomer or copolymer materials as fabric treatment agents that can impart fabric appearance and integrity benefits to fabrics and textiles laundered in washing solutions which contains such materials.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LJ	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

LAUNDRY DETERGENT COMPOSITIONS WITH LINEAR AMINE BASED
POLYMERS TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO
FABRICS LAUNDERED THEREWITH

TECHNICAL FIELD

The present invention relates to compositions, in either liquid or granular form, for use in laundry applications, wherein the compositions comprise certain linear amine based polymer, oligomer or copolymer materials which impart appearance and integrity benefits to fabrics and textiles laundered in washing solutions formed from such compositions.

BACKGROUND OF THE INVENTION

It is, of course, well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles.

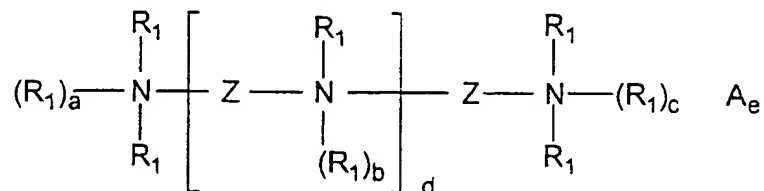
Deterioration of fabric integrity and appearance can manifest itself in several ways. Short fibers are dislodged from woven and knit fabric/textile structures by the mechanical action of laundering. These dislodged fibers may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Further, repeated laundering of fabrics and textiles, especially with bleach-containing laundry products, can remove dye from fabrics and textiles and impart a faded, worn out appearance as a result of diminished color intensity, and in many cases, as a result of changes in hues or shades of color.

Given the foregoing, there is clearly an ongoing need to identify materials which could be added to laundry detergent products that would associate themselves with the fibers of the fabrics and textiles laundered using such detergent products and thereby reduce or minimize the tendency of the laundered fabric/textiles to deteriorate in appearance. Any such detergent product additive material should, of course, be able to benefit fabric appearance and integrity without unduly interfering with the ability of the laundry detergent to perform its fabric cleaning function. The present invention is

directed to the use of linear amine based polymer, oligomer or copolymer materials in laundry applications which perform in this desired manner.

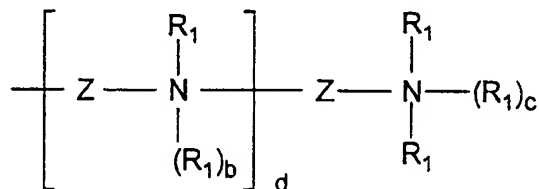
SUMMARY OF THE INVENTION

Linear amine based polymer, oligomer or copolymer materials which are suitable for use in laundry operations and provide the desired fabric appearance and integrity benefits can be characterized by the following general formula:



wherein:

each R_1 is independently selected from the group consisting of H, linear or branched C_1 - C_{12} alkyl, hydroxyalkyl, cycloalkyl, aryl, alkylaryl, piperidinoalkyl and other substituted derivatives of piperidine, morpholinoalkyl and other substituted derivatives of morpholine, substituted derivatives of aryl, substituted derivatives of alkylaryl,



and mixtures thereof;

A is a compatible anion;

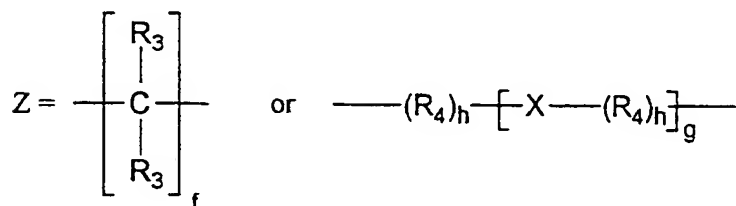
a = 0 or 1;

b = 0 or 1;

c = 0 or 1;

d = from 0 to about 50, preferably from 0 to about 25 and most preferably from about 4 to about 20;

e = number required to obtain charge neutrality;



wherein:

each R_3 is independently selected from the group consisting of H, C_1 - C_{12} alkyl, aryl, alkylaryl, substituted derivatives of aryl, substituted derivatives of alkylaryl, hydroxy, amino, alkoxy, halogen and mixtures thereof;

each R_4 is independently selected from the group consisting of linear or branched alkylene, hydroxyalkylene, and substituted alkylene residues;

X is selected from the group consisting of phenylene, cyclohexylene, substituted residues of phenylene, substituted residues of cyclohexylene, -O-, -COO- and -CON(R_5)-;

R_5 is selected from the group consisting of H, C_1 - C_4 alkyl and hydroxyalkyl;

f = from about 2 to about 12;

g = from about 1 to about 10 when X is -COO- or -CON(R_5)-;

g = from about 1 to about 100 when X is -O-; otherwise

g = 1;

h = 0 or 1;

provided that when one R_3 group is hydroxy or amino, the other R_3 group on the same carbon is not a hydroxy, amino or halogen; and

further provided that within Z no carbon has more than one substituent selected from the group consisting of hydroxy, amino, and halo.

The linear amine based polymer, oligomer or copolymer materials defined above can be used as a washing solution additive in either granular or liquid form. Alternatively, they can be admixed to granular detergents, dissolved in liquid detergent compositions or added to a fabric softening composition. The foregoing description of uses for the linear amine based fabric treatment materials defined herein are intended to be exemplary and other uses will be apparent to those skilled in the art and are intended to be within the scope of the present invention.

The laundry detergent compositions herein comprise from about 1% to 80% by weight of a detergent surfactant, from about 0.1% to 80% by weight of an organic or inorganic detergency builder and from about 0.1% to 5% by weight of the linear amine based fabric treatment materials of the present invention. The detergent surfactant and detergency builder materials can be any of those useful in conventional laundry detergent products.

Aqueous solutions of the linear amine based polymer, oligomer or copolymer materials of the subject invention comprise from about 0.1% to 80% by weight of the

linear amine based fabric treatment materials dissolved in water and other ingredients such as stabilizers and pH adjusters.

In its method aspect, the present invention relates to the laundering or treating of fabrics and textiles in aqueous washing or treating solutions formed from effective amounts of the detergent compositions described herein, or formed from the individual components of such compositions. Laundering of fabrics and textiles in such washing solutions, followed by rinsing and drying, imparts fabric appearance benefits to the fabric and textile articles so treated. Such benefits can include improved overall appearance, pill/fuzz reduction, antifading, improved abrasion resistance, and/or enhanced softness.

DETAILED DESCRIPTION OF THE INVENTION

As noted, when fabric or textiles are laundered in wash solutions which comprise the linear amine based polymer, oligomer or copolymer materials of the present invention fabric appearance and integrity are enhanced. The linear amine based fabric treatment materials can be added to wash solutions by incorporating them into a detergent composition, a fabric softener or by adding them separately to the washing solution. The linear amine based fabric treatment materials are described herein primarily as liquid or granular detergent additives but the present invention is not meant to be so limited. The linear amine based fabric treatment materials, detergent composition components, optional ingredients for such compositions and methods of using such compositions, are described in detail below. All percentages are by weight unless other specified.

A) Linear Amine Based Polymer, Oligomer or Copolymer Materials

The essential component of the compositions of the present invention comprises one or more linear amine based polymer, oligomer or copolymer. Such materials have been found to impart a number of appearance benefits to fabrics and textiles laundered in aqueous washing solutions formed from detergent compositions which contain such linear amine based fabric treatment materials. Such fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against color fading, improved abrasion resistance, etc. The linear amine based fabric treatment materials used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

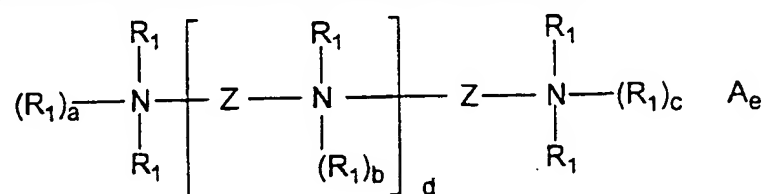
The linear amine based polymer, oligomer or copolymer component of the compositions herein may comprise combinations of these linear amine based materials. For example, a mixture of epichlorohydrine (sometimes referred to herein as "epi") and

hexamethylenediamine condensates (sometimes referred to herein as "HMDA") can be combined with a mixture of bis(hexamethylene)triamine (sometimes referred to herein as "BHMT") and epihalohydrine condensates to achieve the desired fabric treatment results. Moreover, the molecular weight of linear amine based fabric treatment materials can vary within the mixture as is illustrated in the Examples below.

As will be apparent to those skilled in the art, an oligomer is a molecule consisting of only a few monomer units while polymers comprise considerably more monomer units. For the present invention, oligomers are defined as molecules having an average molecular weight below about 1,000 and polymers are molecules having an average molecular weight of greater than about 1,000. Copolymers are polymers or oligomers wherein two or more dissimilar monomers have been simultaneously or sequentially polymerized. Copolymers of the present invention can include, for example, polymers or oligomers polymerized from a mixture of a primary linear amine based monomer, e.g., bis(hexamethylene)triamine, and a secondary linear amine monomer, e.g., epichlorohydrine.

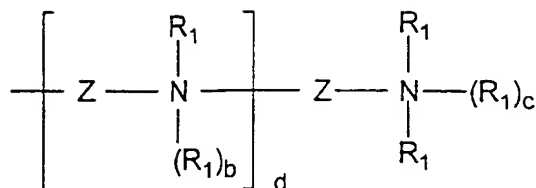
The linear amine based fabric treatment component of the detergent compositions herein will generally comprise from about 0.1% to about 5% by the weight of the detergent composition. More preferably, such linear amine based fabric treatment materials will comprise from about 0.5% to about 4% by weight of the detergent compositions, most preferably from about 0.75% to about 3%. However, as discussed above, when used as a washing solution additive, i.e. when the linear amine based fabric treatment component is not incorporated into a detergent composition, the concentration of the linear amine based component can comprise from about 0.1% to about 80% by weight of the additive material.

One suitable group of linear amine based polymer, oligomer or copolymer materials for use herein is characterized by the following formula:



wherein:

each R_1 is independently selected from the group consisting of H, linear or branched C_1 - C_{12} alkyl, hydroxyalkyl, cycloalkyl, aryl, alkylaryl, piperidinoalkyl and other substituted derivatives of piperidine, morpholinoalkyl and other substituted derivatives of morpholine, substituted derivatives of aryl, substituted derivatives of alkylaryl,



and mixtures thereof;

A is a compatible anion;

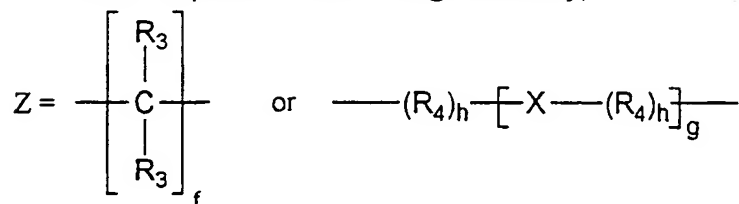
a = 0 or 1;

b = 0 or 1;

c = 0 or 1;

d = from 0 to about 50, preferably from 0 to about 25 and most preferably from about 4 to about 20;

e = number required to obtain charge neutrality;



wherein:

each R_3 is independently selected from the group consisting of H, $\text{C}_1\text{-C}_{12}$ alkyl, aryl, alkylaryl, substituted derivatives of aryl, substituted derivatives of alkylaryl, hydroxy, amino, alkoxy, halogen and mixtures thereof;

each R_4 is independently selected from the group consisting of linear or branched alkylene, hydroxyalkylene, and substituted alkylene residues;

X is selected from the group consisting of phenylene, cyclohexylene, substituted residues of phenylene, substituted residues of cyclohexylene, -O-, -COO- and -CON(R_5)-;

R_5 is selected from the group consisting of H, $\text{C}_1\text{-C}_4$ alkyl and hydroxyalkyl;

f = from about 2 to about 12;

g = from about 1 to about 10 when X is -COO- or -CON(R_5)-;

g = from about 1 to about 100 when X is -O-; otherwise

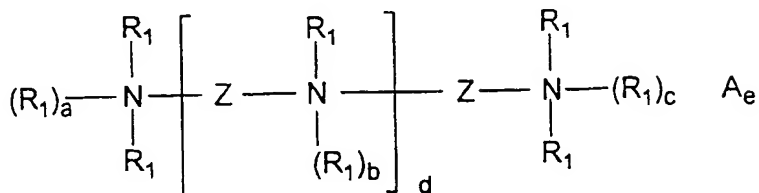
g = 1;

h = 0 or 1;

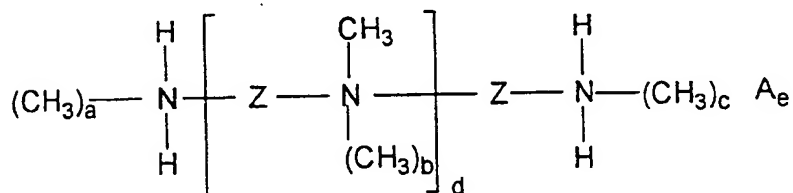
provided that when one R_3 group is hydroxy or amino, the other R_3 group on the same carbon is not a hydroxy, amino or halogen; and

further provided that within Z no carbon has more than one substituent selected from the group consisting of hydroxy, amino, and halo.

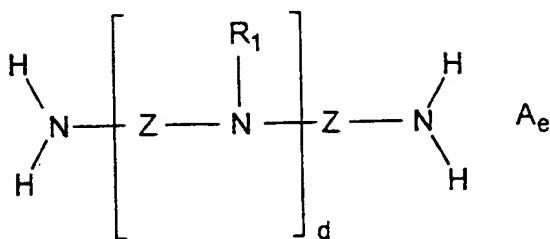
Preferred compounds include those defined below by the simplified structures and examples.



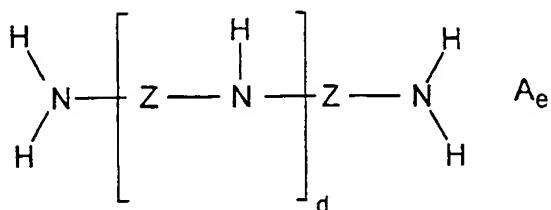
R1	a/b/c	Z	d	Example
CH ₃	0	-(CH ₂) ₆ -	0	Methylated HMDA
CH ₃	0	-(CH ₂) ₆ -	1	Methylated BHMT
CH ₃	1	-(CH ₂) ₆ -	0	Quaternized HMDA
CH ₃	1	-(CH ₂) ₆ -	1	Quaternized BHMT
CH ₂ CH ₂ OH or H	0	-CH ₂ -CH ₂ -CH ₂ - or -CH ₂ -CH(OH)-CH ₂	2-8	aminopropyldiethanolamine:epi, d depends on the ratio of amine:epi
CH ₃ -CH ₂ or H	0	-(CH ₂) ₃ -CH-(CH ₃)- or -CH ₂ -CH(OH)-CH ₂	2-12	2 amino 5diethylaminopentane: epi, d depends on the ratio of amine:epi



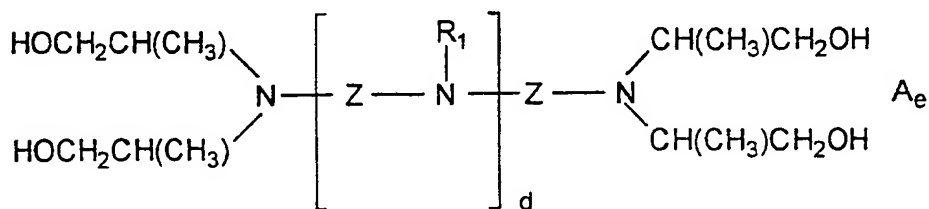
a/b/c	Z	d	Example
0 or 1	-(CH ₂) ₆ -	6	Ionene polymer made by condensation of NNNN tetramethyl hexamethylenediamine and 1,6 dibromo hexane (ratio 4:3)
0 or 1	-(CH ₂) ₆ - or -(CH ₂) ₁₂ -	6	Ionene polymer made by condensation of NNNN tetramethyl hexanediamine and 1,6 dibromo dodecane (ratio 4:3)
0 or 1	-(CH ₂) ₆ -	4	Ionene polymer made by condensation of NNNN tetramethyl hexamethylenediamine and 1,6 dibromo hexane (ratio 3:2)



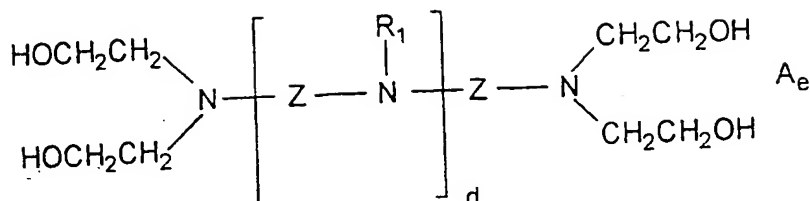
R ₁	Z	d	Example
-(CH ₂) ₃ -NH ₂	-CH ₂ -CH ₂ -CH ₂ -CH ₂ - or -CH ₂ -CH ₂ -CH ₂	2	NNNN tetrakis(aminopropyl) butanediamine
-(CH ₂) ₃ -NH ₂	-(CH ₂) ₆ - or -CH ₂ -CH ₂ -CH ₂	2	NNNN tetrakis(aminopropyl) Hexanediamine
H or CH ₃	-CH ₂ -CH ₂ -CH ₂ - or -CH ₂ -CH(OH)-CH ₂	4-12	N, N bis(3-aminopropyl)methylamine:epi, d depends on the ratio of amine:epi



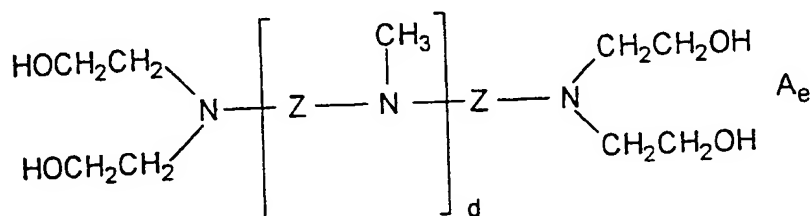
Z	d	Example
-(CH ₂) ₆ - or -CH ₂ -CH(OH)-CH ₂ -	1-10	HMDA-epi, m depends on the ratio of HMDA:epi d = 1 if HMDA:epi are in the ratio of 2:1
-(CH ₂) ₆ - or -CH ₂ -CH(OH)-CH ₂ -	4-12	BHMT-epi, m depends on the ratio of BHMT:epi d = 1 if BHMT:epi are in the ratio of 2:1
-CH ₂ -CH ₂ -CH ₂ -	0	propanediamine
-(CH ₂) ₆ -	0	hexamethylenediamine
-(CH ₂) ₈ -	0	octanediamine
-CH ₂ -CH ₂ -CH ₂ -	1	dipropylenetriamine
-(CH ₂) ₆ -	1	Bis(hexamethylene)triamine
-CH ₂ -CH ₂ - or -CH ₂ -CH ₂ -CH ₂ -	1	2 aminoethyl 1, 3 propane diamine
-CH ₂ -CH ₂ - or -CH ₂ -CH-(CH ₃)-CH ₂ -	1	2 aminoethyl 1, 2 propane diamine
-CH ₂ -CH ₂ - or -CH ₂ -CH ₂ -CH ₂ -	2	bis(aminopropyl)ethylene diamine



R1	Z	d	Example
CH(CH ₃)CH ₂ OH	-(CH ₂) ₆ -	1	Hydroxypropylated BHMT
CH(CH ₃)CH ₂ OH	-(CH ₂) ₆ - or -CH ₂ -CH(OH)-CH ₂	2-8	Hydroxypropyl BHMT-epi
CH(CH ₃)CH ₂ OH or CH ₃	-(CH ₂) ₃ -CH-(CH ₃)- or -CH ₂ -CH(OH)-CH ₂	4-12	Hydroxypropyl N, N bis(3aminopropyl) methylamine:epi



R1	Z	d	Example
CH ₂ CH ₂ OH	-(CH ₂) ₆ -	1	Hydroxyethylated BHMT
CH ₂ CH ₂ OH	-(CH ₂) ₆ - or -CH ₂ -CH(OH)-CH ₂	4-12	Hydroxyethylated BHMT-epi
CH ₂ CH ₂ OH	-CH ₂ -CH ₂ -CH ₂ - or -CH ₂ -CH(OH)-CH ₂	2-8	Hydroxyethylated aminopropyl diethanolamine:epi
CH ₂ CH ₂ OH or CH ₃	-CH ₂ -CH ₂ -CH ₂ - or -CH ₂ -CH(OH)-CH ₂	4-12	Hydroxyethylated N, N bis(3aminopropyl)methylamine:epi
CH ₂ -CH ₂ -OH	-(CH ₂) ₃ -CH-(CH ₃)- or -CH ₂ -CH(OH)-CH ₂	2	Hydroxyethylated 2 amino 5 diethylaminopentane
CH(CH ₃)CH ₂ OH	-CH ₂ -CH ₂ -CH ₂ - or -CH ₂ -CH(OH)-CH ₂	4-12	Hydroxypropyl aminopropyl diethanolamine:epi



Z	d	Example
-(CH ₂) ₆ -	1	Methyl quat of hydroxyethyl BHMT
-CH ₂ -CH ₂ -CH ₂ - or -CH ₂ -CH(OH)-CH ₂	2	Methyl quat of Hydroxyethylated BHMT-epi

Preferred compounds to be used as the linking group Z include, but are not limited to: polyepoxides, ethylenecarbonate, propylenecarbonate, urea, α , β -unsaturated carboxylic acids, esters of α , β -unsaturated carboxylic acids, amides of α , β -unsaturated carboxylic acids, anhydrides of α , β -unsaturated carboxylic acids, di- or polycarboxylic acids, esters of di- or polycarboxylic acids, amides of di- or polycarboxylic acids, anhydrides of di- or polycarboxylic acids, glycidylhalogens, chloroformic esters, chloroacetic esters, derivatives of chloroformic esters, derivatives of chloroacetic esters, epihalohydrins, glycerol dichlorohydrins, bis-(halohydrins), polyetherdihalo-compounds, phosgene, polyhalogens, functionalized glycidyl ethers and mixtures thereof. Moreover, Z can also comprise a reaction product formed by reacting one or more of polyetherdiamines, alkylenediamines, polyalkylenepolyamines, alcohols, alkylene glycols and polyalkylene glycols with α , β -unsaturated carboxylic acids, esters of α , β -unsaturated

carboxylic acids, amides of α , β -unsaturated carboxylic acids and anhydrides of α , β -unsaturated carboxylic acids provided that the reaction products contain at least two double bonds, two carboxylic groups, two amide groups or two ester groups.

B) Deterstive Surfactant

The detergent compositions herein comprise from about 1% to 80% by weight of a deterstive surfactant. Preferably such compositions comprise from about 5% to 50% by weight of surfactant. Deterstive surfactants utilized can be of the anionic, nonionic, zwitterionic, ampholytic or cationic type or can comprise compatible mixtures of these types. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. All of these patents are incorporated herein by reference. Of all the surfactants, anionics and nonionics are preferred.

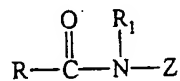
Useful anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Additional non-soap anionic surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, and ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are a) the sodium, potassium and ammonium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; b) the sodium, potassium and ammonium alkyl polyethoxylate sulfates, particularly those in which the alkyl group contains from 10 to 22, preferably from 12 to 18 carbon atoms, and wherein the polyethoxylate chain contains from 1 to 15, preferably 1 to 6 ethoxylate moieties; and c) the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable

are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C₁₁₋₁₃ LAS.

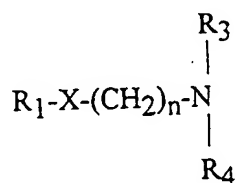
Preferred nonionic surfactants are those of the formula R₁(OC₂H₄)_nOH, wherein R₁ is a C₁₀-C₁₆ alkyl group or a C₈-C₁₂ alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products of C₁₂-C₁₅ alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C₁₂-C₁₃ alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula:

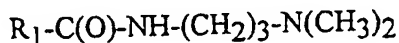
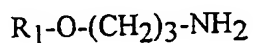
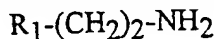


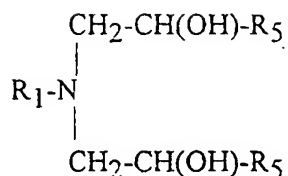
wherein R is a C₉₋₁₇ alkyl or alkenyl, R₁ is a methyl group and Z is glyceryl derived from a reduced sugar or alkoxyated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures of which are incorporated herein by reference.

Preferred surfactants for use in the detergent compositions described herein are amine based surfactants of the general formula:



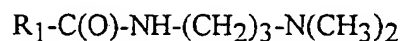
wherein R₁ is a C₆-C₁₂ alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R₃ and R₄ are individually selected from H, C₁-C₄ alkyl, or (CH₂-CH₂-O(R₅)) wherein R₅ is H or methyl. Especially preferred amines based surfactants include the following:





wherein R_1 is a $\text{C}_6\text{-C}_{12}$ alkyl group and R_5 is H or CH_3 . Particularly preferred amines for use in the surfactants defined above include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, $\text{C}_8\text{-C}_{12}$ bis(hydroxyethyl)amine, $\text{C}_8\text{-C}_{12}$ bis(hydroxyisopropyl)amine, $\text{C}_8\text{-C}_{12}$ amido-propyl dimethyl amine, or mixtures thereof.

In a highly preferred embodiment, the amine based surfactant is described by the formula:



wherein R_1 is $\text{C}_8\text{-C}_{12}$ alkyl.

C) Detergent Builder

The detergent compositions herein may also comprise from about 0.1% to 80% by weight of a detergent builder. Preferably such compositions in liquid form will comprise from about 1% to 10% by weight of the builder component. Preferably such compositions in granular form will comprise from about 1% to 50% by weight of the builder component. Detergent builders are well known in the art and can comprise, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al., both of which are incorporated herein by reference. Particularly preferred polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate

and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Examples of suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates. Particularly preferred are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Also preferred are aluminosilicates including zeolites. Such materials and their use as detergent builders are more fully discussed in Corkill et al., U. S. Patent No. 4,605,509, the disclosure of which is incorporated herein by reference. Also discussed in U. S. Patent No. 4,605,509 are crystalline layered silicates which are suitable for use in the detergent compositions of this invention.

D) Optional Detergent Ingredients

In addition to the surfactants, builders and linear amine based polymer, oligomer or copolymer materials hereinbefore described, the detergent compositions of the present invention can also include any number of additional optional ingredients. These include conventional detergent composition components such as enzymes and enzyme stabilizing agents, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, bleaching agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, organic and inorganic fillers, solvents, hydrotropes, optical brighteners, dyes and perfumes.

pH adjusting agents may be necessary in certain applications where the pH of the wash solution is greater than about 10.0 because the fabric integrity benefits of the defined compositions begin to diminish at a higher pH. Hence, if the wash solution is greater than about 10.0 after the addition of the linear amine based polymer, oligomer or copolymer materials of the present invention a pH adjuster should be used to reduce the pH of the washing solution to below about 10.0, preferably to a pH of below about 9.5 and most preferably below about 7.5. Suitable pH adjusters will be known to those skilled in the art.

A preferred optional ingredients for incorporation into the detergent compositions herein comprises a bleaching agent, e.g., a peroxygen bleach. Such peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

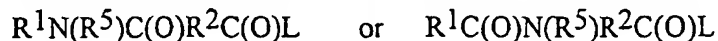
Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-

nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published February 20, 1985; and U.S. Patent 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used, generally in particulate form, in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials. For example, sodium perborate (e.g. mono- or tetra-hydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interlox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical and preferred. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

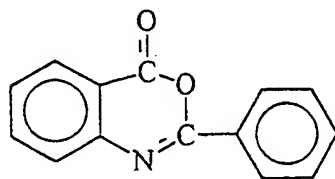
Other useful amido-derived bleach activators are those of the formulae:



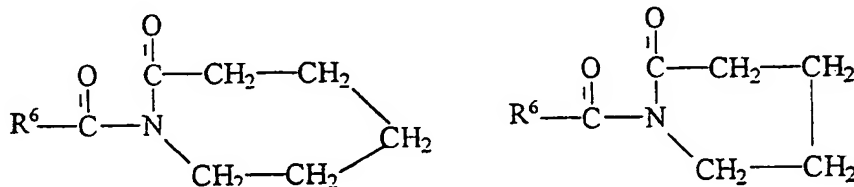
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenol sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551.

Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966, 723, Issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of useful bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, nonanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, Issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

If utilized, peroxygen bleaching agent will generally comprise from about 2% to 30% by weight of the detergent compositions herein. More preferably, peroxygen bleaching agent will comprise from about 2% to 20% by weight of the compositions. Most preferably, peroxygen bleaching agent will be present to the extent of from about 3% to 15% by weight of the compositions herein. If utilized, bleach activators can comprise from about 2% to 10% by weight of the detergent compositions herein.

Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1.

Another highly preferred optional ingredient in the detergent compositions herein is a deterative enzyme component. Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability, optimal thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Deterative enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry detergent composition. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases, amylases and peroxidases.

Enzymes are normally incorporated into detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in

EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 10. U.S. 4,435,307, Barbesgoard et al., March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-OS-2,247,832. CAREZYME® and CELLUZYME® (Novo) are especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in GB 1,372,034. See also, the lipase in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein.

The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the deterative enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and

are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

E) Detergent Composition Preparation

The detergent compositions according to the present invention can be in liquid, paste or granular form. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by any conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients, e.g., surfactants, builders, water, etc., as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The remaining dry ingredients, e.g., granules of the essential linear amine based fabric treatment materials, can be admixed in granular powder form with the spray dried granules in a rotary mixing drum. The liquid ingredients, e.g., solutions of the essential linear amine based fabric treatment materials, enzymes, binders and perfumes, can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Addition of the linear amine based polymer, oligomer or copolymer materials to liquid detergent or other aqueous compositions of this invention may be accomplished by simply mixing into the liquid solutions the desired linear amine based fabric treatment materials.

F) Fabric Laundering Method

The present invention also provides a method for laundering fabrics in a manner which imparts fabric appearance benefits provided by the linear amine based polymer, oligomer or copolymer materials used herein. Such a method employs contacting these

fabrics with an aqueous washing solution formed from an effective amount of the detergent compositions hereinbefore described or formed from the individual components of such compositions. Contacting of fabrics with washing solution will generally occur under conditions of agitation although the compositions of the present invention may also be used to form aqueous unagitated soaking solutions for fabric cleaning and treatment. As discussed above, it is preferred that the washing solution have a pH of less than about 10.0, preferably it has a pH of about 9.5 and most preferably it has a pH of about 7.5.

Agitation is preferably provided in a washing machine for good cleaning. Washing is preferably followed by drying the wet fabric in a conventional clothes dryer. An effective amount of a high density liquid or granular detergent composition in the aqueous wash solution in the washing machine is preferably from about 500 to about 7000 ppm, more preferably from about 1000 to about 3000 ppm.

G) Fabric Conditioning

The linear amine based polymer, oligomer or copolymer materials hereinbefore described as components of the laundry detergent compositions herein may also be used to treat and condition fabrics and textiles in the absence of the surfactant and builder components of the detergent composition embodiments of this invention. Thus, for example, a fabric conditioning composition comprising only the linear amine based fabric treatment materials themselves, or comprising an aqueous solution of the linear amine based fabric treatment materials, may be added during the rinse cycle of a conventional home laundering operation in order to impart the desired fabric appearance and integrity benefits hereinbefore described.

EXAMPLES

The following examples illustrate the compositions and methods of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

EXAMPLE I

The synthesis of one preferred compound of the present invention is described below. Those skilled in the art will be able to modify this description to synthesize other compounds without undue experimentation.

Synthesis of 2:1 Bis(hexamethylene)triamine:Epichlorohydrin Oligomer

Prepare a 2L, three neck, round bottom flask equipped with a magnetic stirring bar, condenser, addition funnel, thermometer, and temperature controller (Therm-O-Watch, I²R). Add to the flask bis(hexamethylene)triamine (Aldrich, ren Hildebrand

Elisabeth Kappes 713.5g, 3.3 mol) and methanol (Baker, approximately 400ml). The solution is blanketed with argon and heated to reflux. Epichlorohydrin (Aldrich, 153.2g, 1.66 mol) is added neat over approximately 45 minutes. The solution is heated at reflux overnight. A ^{13}C -NMR (dmso- d_6) shows the absence of peaks corresponding to epichlorohydrin at approximately 45ppm, approximately 46ppm, and approximately 51ppm. A new peak will appear at approximately 50ppm along with many more new peaks in the 54-70 ppm region. The resulting bulk material is divided into four 1L round bottom flasks and each flask is heated in a Kugelrohr apparatus (Aldrich) at 170°C and approximately 2mmHg for 2 hrs. as methanol and unreacted bis(hexamethylene)triamine distill from the mixture. After cooling, 719g of product is recovered as a tan waxy solid. A ^{13}C -NMR on this thoroughly stripped and heated sample shows peaks at approximately 50ppm and a simplified 54-70 ppm region with peaks at 54.6, 55, 60, 67.7, and 68.6ppm which are consistent with 2-hydroxy-1,3-propylene-linked amines.

In a preferred variation of the above synthesis, a more easily soluble product is formed by ensuring better mixing as the epichlorohydrin is added by diluting the epichlorohydrin with solvent and stirring more vigorously. In another preferred variation, the reaction mixture is heated to about 150-180°C before applying vacuum. This allows any azetidine intermediates to further react in the presence of the excess bis(hexamethylene)triamine prior to its being removed by stripping.

Base liquid and granular detergent compositions were prepared. Various linear amine based polymer, oligomer or copolymer materials were added to the base detergent compositions as described below.

EXAMPLE II

Granular Detergent Test Composition Preparation

Several granular detergent compositions are prepared containing various linear amine based polymer, oligomer or copolymer materials. Such granular detergent compositions all have the following formulas:

<u>Component</u>	<u>Example 1</u> <u>Wt%</u>	<u>Example 2</u> <u>Wt%</u>
C ₁₂ Linear alkyl benzene sulfonate	9.40	9.40
C ₁₄₋₁₅ alkyl sulfonate	11.26	11.26
Zeolite Builder	27.79	27.79
Sodium Carbonate	27.31	27.31
PEG 4000	1.60	1.60
Dispersant	2.26	2.26

C ₁₂₋₁₃ alkyl ethoxylate (E9)	1.5	1.5
Sodium Perborate	1.03	1.03
Soil Release Polymer	0.41	0.41
Enzymes	0.46	0.46
Condensate of bis(hexamethylene)triamine and epichlorohydrin from Example I	0.8	1.6
Perfume, Brightener, Suds Suppressor, Other Minors, Moisture, Sulfate	<u>Balance</u>	<u>Balance</u>
	100%	100%

<u>Component</u>	<u>Examples 3-22</u> <u>Wt%</u>
C ₁₂ Linear alkyl benzene sulfonate	9.31
C ₁₄₋₁₅ alkyl sulfonate	12.74
Zeolite Builder	27.79
Sodium Carbonate	27.31
PEG 4000	1.60
Dispersant	2.26
C ₁₂₋₁₃ alkyl ethoxylate (E9)	1.5
Sodium Perborate	1.03
Soil Release Polymer	0.41
Enzymes	0.59
Polymer/oligomer as in TABLE II	See Table II
Perfume, Brightener, Suds Suppressor, Other Minors, Moisture, Sulfate	<u>Balance</u>
	100%

TABLE II

#	Polymer*	wt. %
3	Bis(hexamethylene)triamine	1.6
4	Bis(hexamethylene)triamine	3.2
5	Adduct of Aminopropyldiethanolamine and epi (ratio 2:1)	0.8
6	Adduct of N,N bis(3-aminopropyl)methylamine and epi (Ratio 2:1)	0.8
7	Adduct of N-(2 -Aminoethyl) ethanolamine and epi (Ratio 2:1)	0.8
8	Adduct of N,N bis(aminopropyl)ethylenediamine and epi (Ratio 2:1)	0.8
9	Diproporylenetriamine-epi 2:1	0.8
10	Adduct of 2 amino-5 (diethylamino) pentane and epi (ratio 2:1)	0.8
11	Adduct of Diethylaminoethylamine and epi (Ratio 2:1)	0.8
12	Adduct of 2(ethylamino) ethyleneamine and epi (Ratio 1.5:1)	0.8

13	Adduct of 4,9 Dioxadodecane, 1,12 diamine and epi (Ratio 2:1)	0.8
14	Adduct of 4,7,10 trioxitridecan 1, 13 diamine and epi (Ratio 1.5:1)	0.8
15	Oligomer made by condensation of N,N,N',N' tetramethyl 1,6 hexamethylenediamine and 1,6 dibromo hexane (ratio 4:3)	3.0
16	Oligomer made by condensation of N,N,N',N' tetramethyl 1, 6 hexanediamine and 1,6 dibromo dodecane (ratio 4:3)	3.0
17	Oligomer made by condensation of N,N,N',N' tetramethyl 1,6 hexamethylenediamine and 1,6 dibromo hexane (ratio 2:1)	3.0
18	Oligomer made by condensation of N,N,N',N' tetramethyl 1,6 hexamethylenediamine and 1,6 dibromo hexane (ratio 3:2)	3.0
19	Methylated adduct of bis(hexamethylene)triamine	1.1
20	Hydroxypropyl N, N bis(3aminopropyl) methylamine:epi (2:1)	0.8
21	Hydroxyethyl N, N bis(3aminopropyl) methylamine:epi (2:1)	1.4
22	Hydroxyethyl bis(hexamethylene)triamine adduct	0.8

EXAMPLE III

Liquid Detergent Compositions

Several liquid detergent compositions are prepared containing various linear amine based polymer, oligomer or copolymer materials. Such liquid detergent compositions all have the following formulas:

<u>Component</u>	<u>Examples</u> 24-31 Wt. %
C ₁₂₋₁₅ alkyl ether (2.5) sulfate	19.0
C ₁₂₋₁₃ alkyl ethoxylate (9.0)	2.00
C ₁₂₋₁₄ glucose amide	3.50
Citric Acid	3.00
C ₁₂₋₁₄ Fatty Acid	2.00
MEA	to pH 8
Ethanol	3.4
Propanediol	6.51
Borax	2.5
Dispersant	1.18
Na Toluene Sulfonate	2.50
Oligomer and/or polymer as shown in Table III	as in Table III
Dye, Perfume, Brighteners, Enzymes, Preservatives, Suds Suppressor, Other Minors, Water	<u>Balance</u>
	100%

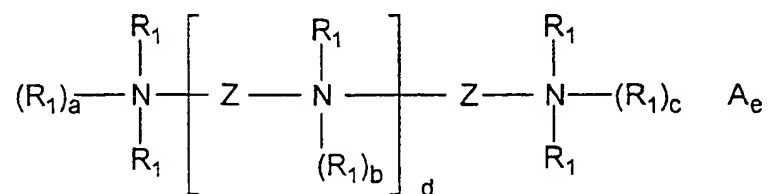
TABLE III

#	Polymer*	wt. %
24	Bis(hexamethylene)triamine	0.5
25	Adduct of Bis(hexamethylene)triamine and epichlorohydrin (ratio 2:1)	0.5
26	Adduct of Bis(hexamethylene)triamine and epichlorohydrin (ratio 1.5:1)	0.5
27	N(3 aminopropyl)1,3 propanediamine	0.5
28	N-(2 aminoethyl)1,3 propanediamine	0.5
29	N, N' bis(3 aminopropyl) ethylenediamine	0.5
30	N,N,N',N'-tetrakis(aminopropyl) butanediamine	2.0
31	Dendrimer Generation 2	2.0

What is claimed is:

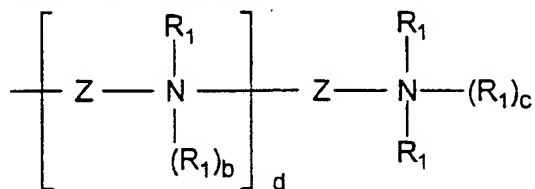
1. A detergent composition comprising:

- a) from about 1% to about 80% by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric surfactants, or mixtures thereof; and
- b) from about 0.1% to about 5.0% by weight of a mixture of linear amine based polymers, oligomers or copolymers of the general formula:



wherein:

each R_1 is independently selected from the group consisting of H, linear or branched C_1 - C_{12} alkyl, hydroxyalkyl, cycloalkyl, aryl, alkylaryl, piperidinoalkyl and other substituted derivatives of piperidine, morpholinoalkyl and other substituted derivatives of morpholine, substituted derivatives of aryl, substituted derivatives of alkylaryl,



and mixtures thereof;

A is a compatible anion;

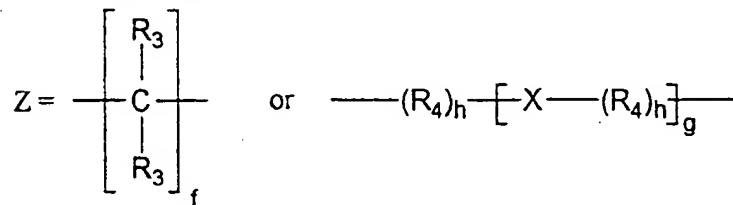
a = 0 or 1;

b = 0 or 1;

c = 0 or 1;

d = from 0 to about 50;

e = number required to obtain charge neutrality;



wherein:

each R_3 is independently selected from the group consisting of H, C_1 - C_{12} alkyl, aryl, alkylaryl, substituted derivatives of aryl, substituted derivatives of alkylaryl, hydroxy, amino, alkoxy, halogen and mixtures thereof;

each R_4 is independently selected from the group consisting of linear or branched alkylene, hydroxyalkylene, and substituted alkylene residues;

X is selected from the group consisting of phenylene, cyclohexylene, substituted residues of phenylene, substituted residues of cyclohexylene, -O-, -COO- and -CON(R_5)-;

R_5 is selected from the group consisting of H, C_1 - C_4 alkyl and hydroxyalkyl;

f = from about 2 to about 12;

g = from about 1 to about 10 when X is -COO- or -CON(R_5)-;

g = from about 1 to about 100 when X is -O-; otherwise

g = 1;

h = 0 or 1;

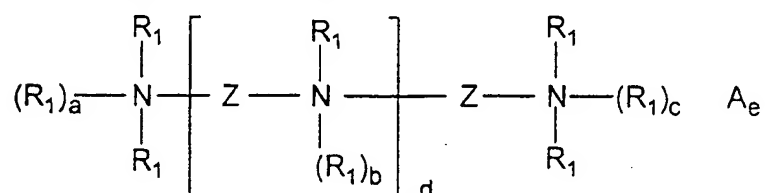
provided that when one R_3 group is hydroxy or amino, the other R_3 group on the same carbon is not a hydroxy, amino or halogen; and

further provided that within Z no carbon has more than one substituent selected from the group consisting of hydroxy, amino, and halo.

2. A composition according to Claim 1, wherein R_1 is selected from the group consisting of -H, -CH₃, -CH₂CH₃, -(CH₂)NH₂, -CH₂CH₂OH, -CH(CH₃)CH₂OH and mixtures thereof.
3. A composition according to either of Claims 1 or 2, wherein R_2 if present is selected from the group consisting of -H, -CH₃, and mixtures thereof.
4. A composition according to any of Claims 1-3, wherein Z is selected from the group consisting of -(CH₂)_x-, -CH₂CHOHCH₂-, -(CH₂)₃CH(CH₃)-, and mixtures thereof, where x is from about 2 to about 12.

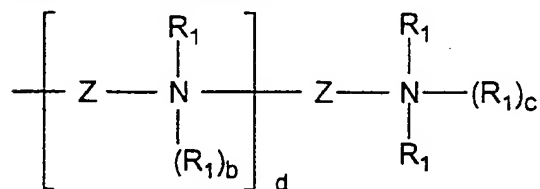
5. A laundry additive composition comprising:

- a) from about 1% to about 80% by weight of water; and
- b) from about 0.1% to about 80.0% by weight of a mixture of linear amine based polymers, oligomers or copolymers of the general formula:



wherein:

each R_1 is independently selected from the group consisting of H, linear or branched C_1 - C_{12} alkyl, hydroxyalkyl, cycloalkyl, aryl, alkylaryl, piperidinoalkyl and other substituted derivatives of piperidine, morpholinoalkyl and other substituted derivatives of morpholine, substituted derivatives of aryl, substituted derivatives of alkylaryl,



and mixtures thereof;

A is a compatible anion;

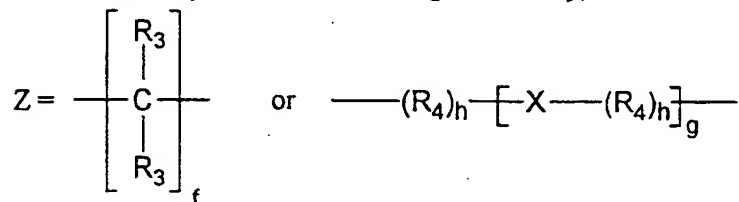
a = 0 or 1;

b = 0 or 1;

c = 0 or 1;

d = from 0 to about 50;

e = number required to obtain charge neutrality;



wherein:

each R_3 is independently selected from the group consisting of H, C_1 - C_{12} alkyl, aryl, alkylaryl, substituted derivatives of aryl, substituted derivatives of alkylaryl, hydroxy, amino, alkoxy, halogen and mixtures thereof;

each R_4 is independently selected from the group consisting of linear or branched alkylene, hydroxyalkylene, and substituted alkylene residues;

X is selected from the group consisting of phenylene, cyclohexylene, substituted residues of phenylene, substituted residues of cyclohexylene, -O-, -COO- and -CON(R₅)-;

R₅ is selected from the group consisting of H, C₁-C₄ alkyl and hydroxyalkyl;

f = from about 2 to about 12;

g = from about 1 to about 10 when X is -COO- or -CON(R₅)-;

g = from about 1 to about 100 when X is -O-; otherwise

g = 1;

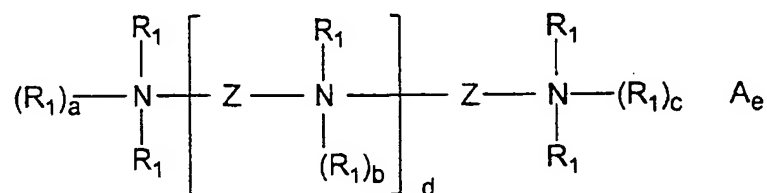
h = 0 or 1;

provided that when one R₃ group is hydroxy or amino, the other R₃ group on the same carbon is not a hydroxy, amino or halogen; and

further provided that within Z no carbon has more than one substituent selected from the group consisting of hydroxy, amino, and halo.

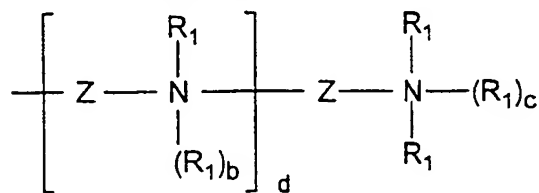
6. A composition according to Claim 5, wherein R₁ is selected from the group consisting of -H, -CH₃, -CH₂CH₃, -(CH₂)NH₂, -CH₂CH₂OH, -CH(CH₃)CH₂OH, and mixtures thereof.

7. A linear amine based polymer, oligomer or copolymer of general formula:



wherein:

each R₁ is independently selected from the group consisting of H, linear or branched C₁-C₁₂ alkyl, hydroxyalkyl, cycloalkyl, aryl, alkylaryl, piperidinoalkyl and other substituted derivatives of piperidine, morpholinoalkyl and other substituted derivatives of morpholine, substituted derivatives of aryl, substituted derivatives of alkylaryl,



and mixtures thereof,

A is a compatible anion;

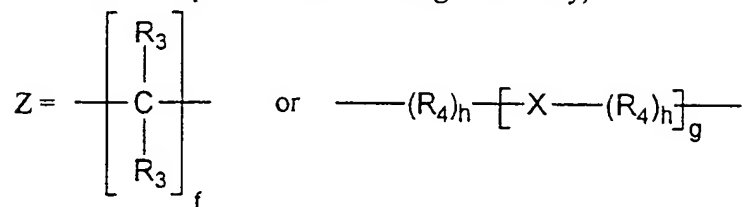
a = 0 or 1;

b = 0 or 1;

c = 0 or 1;

d = from 0 to about 50;

e = number required to obtain charge neutrality;



wherein:

each R_3 is independently selected from the group consisting of H, C_1 - C_{12} alkyl, aryl, alkylaryl, substituted derivatives of aryl, substituted derivatives of alkylaryl, hydroxy, amino, alkoxy, halogen and mixtures thereof;

each R_4 is independently selected from the group consisting of linear or branched alkylene, hydroxyalkylene, and substituted alkylene residues;

X is selected from the group consisting of phenylene, cyclohexylene, substituted residues of phenylene, substituted residues of cyclohexylene, -O-, -COO- and -CON(R_5)-;

R_5 is selected from the group consisting of H, C_1 - C_4 alkyl and hydroxyalkyl;

f = from about 2 to about 12;

g = from about 1 to about 10 when X is -COO- or -CON(R_5)-;

g = from about 1 to about 100 when X is -O-; otherwise

g = 1;

h = 0 or 1;

provided that when one R_3 group is hydroxy or amino, the other R_3 group on the same carbon is not a hydroxy, amino or halogen; and

further provided that within Z no carbon has more than one substituent selected from the group consisting of hydroxy, amino, and halo.

8. A linear amine based polymer, oligomer or copolymer mixture produced by reacting a reaction mixture comprising a linear amine and a polymerizable compound in a predetermined molar ratio of linear amine:polymerizable compound.
9. A compound according to Claim 8, wherein d is from 0 to about 25.

10. A compound according to either Claim 8 or 9, wherein d is from about 4 to about 20.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/19140

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/30 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 761 418 A (PARRAN J) 25 September 1973 see column 7, line 55 - column 8, line 36; claim 1; example XIX ---	1,2,4-10
X	US 5 221 496 A (HOLLAND RICHARD J) 22 June 1993 see claim 1; tables 1,2 ---	1,2,4-9
X	DATABASE WPI Section Ch, Week 8931 Derwent Publications Ltd., London, GB; Class D25, AN 89-225541 XP002083531 & JP 01 162866 A (KAO CORP), 27 June 1989 see abstract ---	1,2,4-7, 9
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 November 1998

Date of mailing of the international search report

02/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/19140

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 065 257 A (COE GERVASE ET AL) 27 December 1977 see column 2, line 21 - line 25 see column 5, line 15 - line 46 see column 7, line 56 - line 65 see claims 1-4,12-14; example 1 ---	1,2,4-9
X	US 4 263 179 A (SCHMOLKA IRVING R) 21 April 1981 see column 2, line 47 - line 63; claims; example 1 ---	1,2,4-9
P,X	WO 97 42286 A (PROCTER & GAMBLE) 13 November 1997 see examples 16,20 ---	1,2,4-9
X	EP 0 232 092 A (GOLDMAN ROBERT ;STEIGMAN JOSEPH DR (US); FRIEDKIN DON S (US)) 12 August 1987 see claims 1,4,13; examples 3,4 -----	1,2,4,7, 9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/19140

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3761418	A	25-09-1973	AT 310905 B	15-09-1973
			BE 721384 A	25-03-1969
			CH 531041 A	30-11-1972
			DE 1792618 A	25-11-1971
			FR 1588952 A	16-03-1970
			GB 1195158 A	17-06-1970
			NL 6813826 A	31-03-1969
			SE 353738 B	12-02-1973
			US 3580853 A	25-05-1971
			US 3723325 A	27-03-1973
			US 3753916 A	21-08-1973
			US 3761417 A	25-09-1973
US 5221496	A	22-06-1993	NONE	
US 4065257	A	27-12-1977	GB 1380133 A	08-01-1975
			AT 163473 A	15-11-1975
			BE 795837 A	23-08-1973
			CH 575463 A	14-05-1976
			DE 2309099 A	30-08-1973
			FR 2173222 A	05-10-1973
			NL 7302589 A	28-08-1973
US 4263179	A	21-04-1981	CA 1134709 A	02-11-1982
			US 4321167 A	23-03-1982
WO 9742286	A	13-11-1997	AU 2743497 A	26-11-1997
			WO 9742287 A	13-11-1997
EP 0232092	A	12-08-1987	AU 590043 B	26-10-1989
			AU 6802687 A	30-07-1987
			JP 1062486 A	08-03-1989